Transport and magnetic properties in multi-walled carbon nanotube ropes: Evidence for superconductivity above room temperature

Guo-meng Zhao*

Department of Physics, Texas Center for Superconductivity and Advanced Materials, University of Houston, Houston, Texas 77204, USA

Detailed analyses are made on previously published data for multi-walled carbon nanotubes. The field dependence of the Hall voltage, the temperature dependence of the Hall coefficient, and the magnetoresistance effect (Phys. Rev. Lett. 72, 697 (1994)) can all be consistently explained in terms of the coexistence of physically separated tubes and Josephson-coupled superconducting tubes with superconductivity above room temperature. The observed temperature dependencies of the remnant magnetization, the diamagnetic susceptibility, and the conductance are consistent with superconductivity above room temperature, but are inconsistent with ferromagnetic contamination. We also interpret the paramagnetic signal and unusual field dependence of the magnetization at 300 K (Phys. Rev. B 49, 15122 (1994)) as arising from the paramagnetic Meissner effect in a multiply connected superconducting network.

Finding room temperature superconductors is one of the most challenging problems in science. It is generally accepted that low temperature superconductivity in simple metals arises from electron-phonon coupling which provides a weak effective attraction for two electrons to pair up. This phonon-mediated pairing mechanism would lead to a superconducting transition temperature T_c lower than 30 K according to McMillan's estimate [1]. The discovery of high-temperature superconductivity at about 40 K in electron-doped C_{60} [2] raises an interesting question of whether the unusually high-T_c superconductivity in this carbon-based material is still mediated by phonons. Alexandrov and Mott [3] estimated that the highest T_c within a strong electron-phonon coupling model is about $\omega/3$, where ω is the characteristic phonon frequency. Because ω in graphite related materials is about 2400 K [4], it is possible to find room temperature superconductivity in graphite-related materials if the electron-phonon coupling could be substantially enhanced. Pokropivny [5] argued that a whispering mode in nanotubes should be responsible for a strong enhancement of electron-phonon interaction, which might lead to room temperature superconductivity. A theoretical calculation showed that superconductivity as high as 500 K can be reached through the pairing interaction mediated by undamped acoustic plasmon modes in a quasi-one-dimensional electronic system [6]. For a multi-layer electronic system such as cuprates and multi-walled carbon nanotubes (MWNTs), high-temperature superconductivity can occur due to an attraction of the carriers in the same conducting layer via exchange of virtual plasmons in neighboring layers [7]. Indeed, a strong coupling of electrons with high-energy ($\sim$ 2 eV) electronic excitations in cuprates has been demonstrated by well-designed optical experiments [8]. These authors also show that the strong coupling between electrons with high-energy electronic excitations along with strong electron-phonon coupling is primarily responsible for superconductivity above 100 K in cuprates [8], in agreement with a recent work [9]. For MWNTs, the dual character of the quasi-one-dimensional and multi-layer electronic structure could lead to a larger pairing interaction via electron-plasmon coupling and thus to superconductivity at higher temperatures. Indeed, magnetic and electrical measurements on multi-walled nanotube ropes [10] have provided subtle evidence for superconductivity above 600 K.

Here we provide detailed analyses on previously published data for multi-walled nanotube ropes. We can consistently explain the temperature dependencies of the Hall coefficient, the magnetoresistance effect, the remnant magnetization, the diamagnetic susceptibility, the conductance, and the field dependence of the Hall voltage [11] in terms of the coexistence of physically separated (PS) tubes and Josephson-coupled (JC) superconducting tubes with superconductivity above room temperature. We also interpret the paramagnetic signal and unusual field dependence of the magnetization at 300 K (Ref. [12]) as arising from the paramagnetic Meissner effect in a multiply connected superconducting network.

We first discuss the temperature dependencies of the remnant magnetization M_r and the diamagnetic susceptibility for our multi-walled nanotube ropes. The experimental results from Ref. [10] are reproduced in Fig. 1. It is apparent that the temperature dependence of M_r (Fig.1a) is similar to that of the diamagnetic susceptibility (Fig.1b) except for the opposite signs. This behavior is expected for a superconductor. A M_r was also observed by Tsebro *et al.* up to 300 K [13]. However, the observation of the M_r alone does not give unambiguous evidence for superconductivity since M_r could be caused by ferromagnetic impurities and/or ballistic transport.

We can now rule out the existence of ferromagnetic impurities. If there were ferromagnetic impurities, the total susceptibility would tend to turn up below 120 K where

the M_r increases suddenly. This is because the paramagnetic susceptibility contributed from the ferromagnetic impurities would increase below 120 K. In contrast, the susceptibility suddenly turns down rather than turns up below 120 K (Fig. 1b). This provides strong evidence that the observed M_r in our nanotubes has nothing to do with the presence of ferromagnetic impurities.

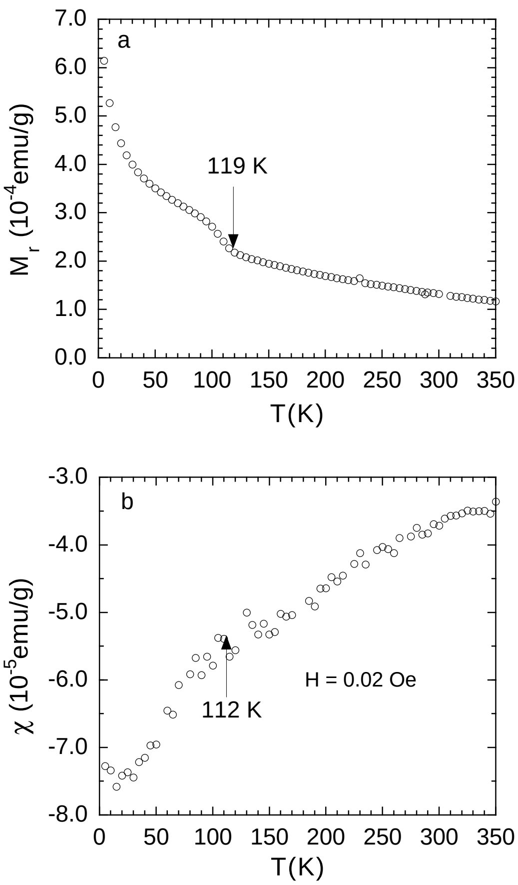

FIG. 1. a) Temperature dependence of the remnant magnetization for multi-walled nanotubes. b) The field-cooled susceptibility as a function of temperature in a field of 0.020 Oe. After Ref. [10].

Fig. 2 shows the temperature dependence of the conductance for a multi-walled nanotube rope, which is reproduced from Ref. [11]. We have found the temperature dependence of the conductance in our nanotube ropes to be nearly the same as that shown in Fig. 2. It is apparent that the slope of the conductance versus temperature curve for the MWNT sample starts to change below 120 K where both the remnant magnetization and the field-cooled diamagnetic signal suddenly increase. This suggests that the magnetic properties are closely related to the electrical transport of the nanotubes.

Alternatively, assuming perfect conductivity, the change in the slope of the conductance below 120 K could be due to the increase in the ballistic conduction channels. However, this scenario cannot consistently account for the observed increase of the field-cooled diamagnetic signal below 120 K since perfect conductors cannot expel magnetic flux in the field-cooled condition.

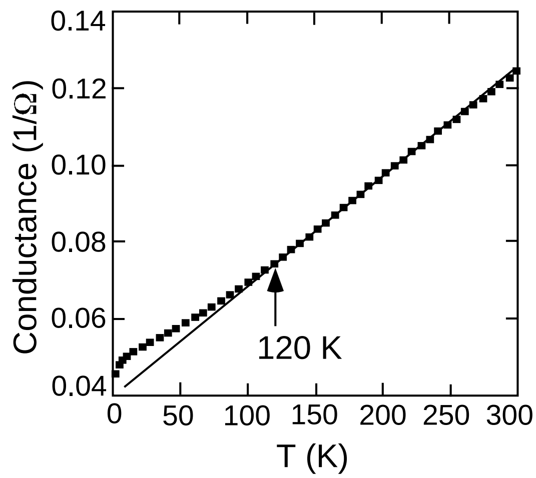

FIG. 2. Temperature dependence of the conductance for a multi-walled nanotube rope, which is reproduced from Ref. [11]. We have found nearly the same temperature dependence of the conductance in our nanotube ropes.

In Fig. 3, we show the temperature dependence of the Hall coefficient (Fig. 3a) and the field dependence of the Hall voltage (Fig. 3b) for a multi-walled nanotube rope. These figures are again reproduced from Ref. [11]. It is striking that the Hall coefficient increases rapidly below about 120 K where the slopes of all three quantities in Fig. 1 and Fig. 2 suddenly change. The fact that such a strong temperature dependence below 120 K was not seen in physically separated tubes [14,15] suggests that this is not an intrinsic property of a single tube, but associated with the coupling of the tubes. Below we will interpret these data in a consistent way by considering the coexistence of physically separated (PS) tubes and Josephson-coupled (JC) superconducting tubes with superconductivity above room temperature.

It is well known that the carbon nanotubes have two types of electronic structures depending on the chirality [16,17], which is indexed by a chiral vector (n, m): $n - m = 3N + \nu$, where N, n, m are the integers, and $\nu = 0, \pm 1$. Tubes with $\nu = 0$ are metallic while undoped tubes with $\nu = \pm 1$ are semiconductive. Multi-walled nanotubes consist of at least two concentric shells which could have different chiralities. Presumably, each shell, if isolated and appropriately doped, should exhibit phase incoherent superconductivity. If the doped shells are nested to form a MWNT such that there is a sufficient number of adjacent superconducting shells that are Josephson coupled, the single MWNT could be-

come a phase coherent non-dissipative superconductor. Similarly, if phase incoherent superconducting tubes are closely packed into a bundle, the bundle could become a phase coherent superconductor via Josephson coupling. It is also possible that some tubes are not superconducting due to insufficient doping.

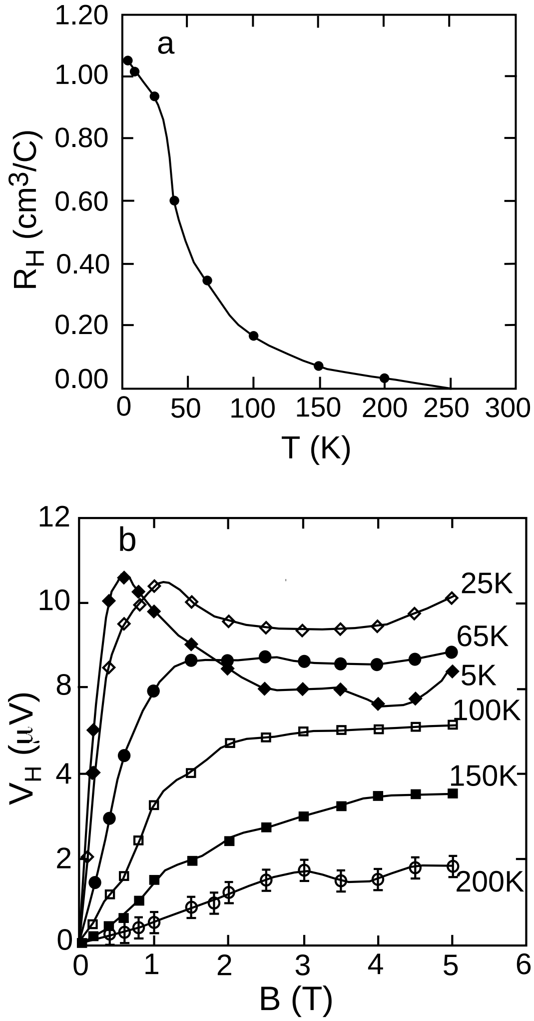

FIG. 3. a) The Hall coefficient versus temperature for a nanotube bundle. b) The Hall voltage as a function of magnetic field measured at different temperatures. The solid lines are drawn to guide the eye. The figures are reproduced from Ref. [11].

We could classify the tubes in a rope into physically separated (PS) tubes and Josephson-coupled (JC) superconducting tubes with superconductivity above room temperature. Since the electronic properties for physically coupled nonsuperconducting bundles containing tubes with random chiralities have no appreciable differences from those for physically separated nonsuperconducting tubes [18], we consider all nonsuperconducting tubes as physically separated tubes.

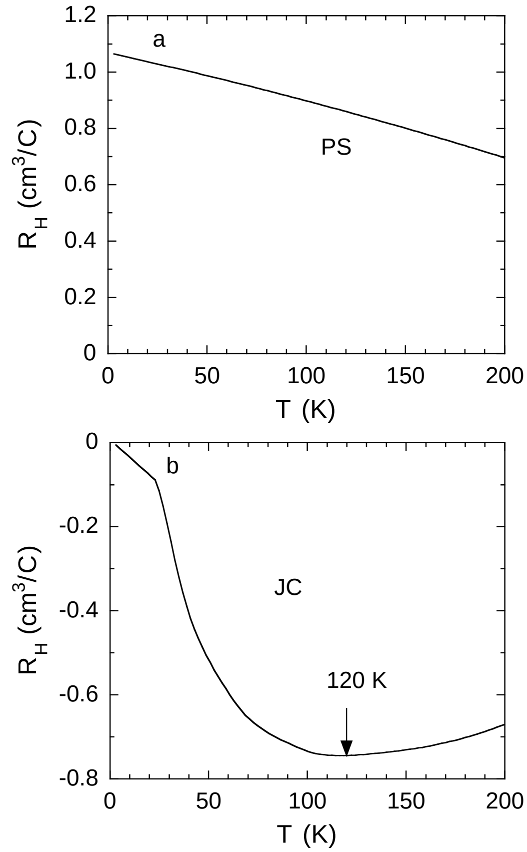

FIG. 4. a) The Hall coefficient component for physically separated tubes (PS). b) The Hall coefficient component for Josephson-coupled superconducting tubes (JC). The sum of both components is taken to be equal to the data of Fig. 3a while the behavior shown in Ref. [14] is used to delineate the PS contribution.

The Hall coefficient for physically separated tubes should be positive, as reported in Ref. [14]. The Hall coefficient for a single non-dissipative superconducting MWNT should be zero because no vortices could be trapped into the single tube whose diameter is much smaller than the intervortex distance. The physically separated nonsuperconducting and phase-incoherent superconducting tubes should have a positive Hall coefficient similar to that in the normal state. On the other hand, vortices can be trapped into Josephson-coupled superconducting tubes, leading to a vortex-liquid state above a characteristic field that depends on the Josephson coupling strength. As seen in both cuprates and MgB_2 [19,20], the low-field Hall coefficient R_H in the vortex-liquid state is negative below T_c, reaches a minimum at T_k and then increases towards zero with further decreasing temperature. Below the characteristic temperature T_k, vortices start to be pinned so that the magnitudes of the Hall conductivity, longitudinal conductivity, the critical current (remnant magnetization), and

diamagnetic susceptibility increase simultaneously. This can naturally explain why the diamagnetic susceptibility, the remnant magnetization, and the Hall coefficient simultaneously increase below about 120 K, as seen from Fig. 1 and Fig. 3a.

We can decompose the total Hall coefficient into two components: one for Josephson-coupled superconducting tubes (JC) and the other for physically separated tubes (PS). The PS component is proportional to the measured Hall coefficient for physically separated tubes [14] with the constraint that, at zero temperature, the magnitude of the PS component is equal to the total Hall coefficient. The JC component is obtained by subtracting the PS component from the total Hall coefficient. Fig. 4 shows both the PS and JC components. It is apparent that the JC component has a local minimum at $T_k \simeq 120$ K, where the total Hall coefficient starts to increase rapidly (see Fig. 3a). The negative value of the JC component remains up to 200 K, suggesting that the superconducting transition temperature is far above 200 K.

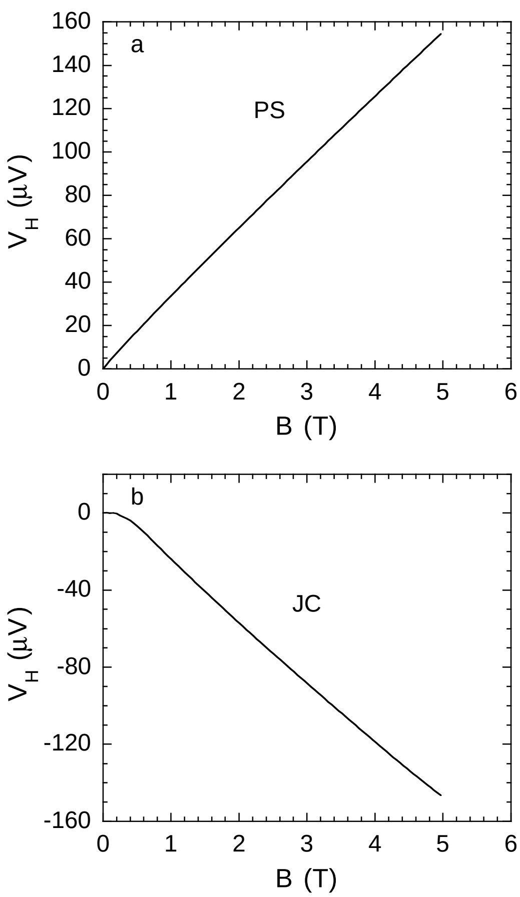

FIG. 5. a) The Hall voltage component for physically separated tubes (PS) at 5 K. b) The Hall voltage component for Josephson-coupled superconducting tubes (JC) at 5 K.

Similarly, as seen in cuprates and MgB_2 [19,20,21], the Hall voltage V_H in the vortex-liquid state is negative, passing through a minimum at B_k, and then increasing towards the normal-state value with further increasing temperature. Below B_o, V_H tends to zero. Interestingly, both B_o and B_k can be independently obtained from the field dependence of the longitudinal resistivity, as described in Ref. [21].

We can also decompose the total Hall voltage into two components: one for Josephson-coupled superconducting tubes (JC) and the other for physically separated tubes (PS). Plotted in Fig. 5a is the PS component at 5 K, which is proportional to the measured Hall voltage for physically separated tubes [14] and matches with the low field data shown in Fig. 3b. Fig. 5b shows the JC component at 5 K, which is obtained by subtracting the PS component from the total Hall voltage. The decomposition was performed after the data in Fig. 3b were smoothed. We can see that the field dependence of the JC component is quite similar to that for cuprates and MgB_2 [19,20,21] except that B_o in the MWNTs is rather small, which may be due to a weak pinning potential. Fig. 5b also indicates that the magnitude of B_k is larger than 5 T. As discussed below, this is in agreement with the longitudinal magnetoresistance data.

Since the contribution from the physically separated tubes is negligible [14], the longitudinal magnetoresistance at 300 K mainly arises from the Josephson-coupled superconducting tubes. From the magnetoresistance data at 300 K [11] and the criterion for determining B_k [21], we find that $B_k \simeq 3.0$ T at 300 K. Using $B_k(T) \propto (1 - T/T_c)^{1.5}$ (Ref. [21]), $B_k(5K) > 5$ T, and $B_k(300K) = 3.0$ T, we find that 300 K$<T_c <$ 1070 K.

Within this two component model, we can also explain the unusual magnetoresistance (MR) effect below 150 K. Because physically separated tubes produce a negative MR effect at low temperatures while the Josephson-coupled superconducting tubes generate a positive MR effect, these opposing contributions from the two components can lead to a local minimum at certain magnetic field. This is indeed the case (see Fig. 1 of Ref. [11]). At high temperatures, the negative MR effect contributed from the physically separated tubes should become weak so that the positive MR effect contributed from the Josephson-coupled superconducting tubes dominates, in agreement with the experimental results [10,11].

There are more experimental results that support the thesis of room temperature superconductivity in multi-walled nanotubes. Fig. 6a shows the temperature dependence of the susceptibility for a MWNT nanotube rope in a field of $H = 400$ Oe, which is reproduced from Ref. [12]. It is striking that the temperature dependence of the susceptibility for the MWNT rope is similar to that for a ceramic cuprate superconductor $Bi_2Sr_2CaCu_2O_{8+y}$ (BSCCO) in a field of $H = 0.02$ Oe (see Fig. 6b which is reproduced from Ref. [22]). By analogy, the observation

of a paramagnetic signal at 300 K could be explained as arising from the paramagnetic Meissner effect below the superconducting transition temperature, as observed in ceramic cuprate superconductors [22] and in multijunction loops of conventional superconductors [23].

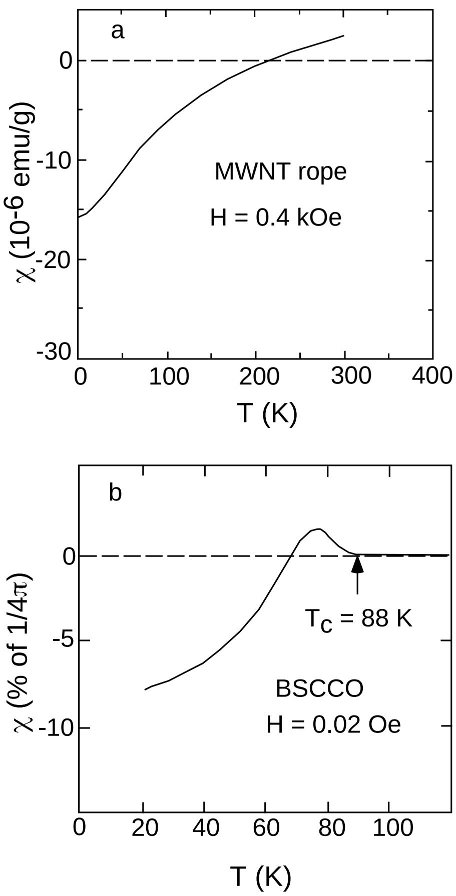

FIG. 6. a) Temperature dependence of the susceptibility for a MWNT nanotube rope in a field of $H = 400$ Oe. The figure is reproduced from Ref. [12]. b) Temperature dependence of the susceptibility of $Bi_2Sr_2CaCu_2O_{8+y}$ (BSCCO) in a field of $H = 0.02$ Oe . The figure is reproduced from Ref. [22].

On the other hand, the observed paramagnetic signal at 300 K and the $M(H)$ curve below $H = 10$ kOe (see Fig. 7 of Ref. [12]) could be compatible with the presence of ferromagnetic impurities. However, such ferromagnetic impurities should be detectable in the high-field magnetization curve by a non-zero intercept in the extrapolation for $H \rightarrow 0$. The intercept was found to be nearly zero at 300 K in the samples of Ref. [12]. In our samples [10] prepared from graphite rods with the same purity (99.9995%) as the ones in Ref. [12], the intercepts are negligible throughout the temperature range of 250 K to 400 K. For the less pure C_{60} and graphite samples of Ref. [12], the contamination of ferromagnetic impurities is clearly seen from the $M(H)$ curve in the high-field range [12]. The clear "ferromagnetic" signal observed only in the low field range [12] is similar to that in the case of granular superconductors [22]. The "ferromagnetic" signal may be caused by a "ferromagnetic" ordering of elementary long-thin current loops [24]. The critical magnetic field below which the "ferromagnetic" state is stable should depend on the number of filaments per current loop. The large critical field of about 10 kOe in the samples of Ref. [12] suggests that a current loop may correspond to a bundle consisting of a large number of tubes.

In summary, we have made detailed analyses on previously published data for multi-walled nanotube ropes. The observed field dependence of the Hall voltage, the temperature dependence of the Hall coefficient, and the magnetoresistance effect can be consistently explained in terms of the coexistence of physically separated tubes and Josephson-coupled superconducting tubes with superconductivity above room temperature. The temperature dependencies of the remnant magnetization, the diamagnetic susceptibility, and the conductance are consistent with superconductivity rather than with ballistic transport or inclusion of ferromagnetic impurities. We also interpret the observed paramagnetic signal and unusual field dependence of the magnetization at 300 K as arising from the paramagnetic Meissner effect in multiply connected room-temperature superconducting network.

Acknowledgment: The author thanks Dr. Pieder Beeli for his critical reading and comments on the manuscript. The author acknowledges financial support from the State of Texas through the Texas Center for Superconductivity and Advanced Materials at the University of Houston where some of the work was completed.

Correspondence should be addressed to gmzhao@uh.edu.

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